



## Composite Membranes for Direct Methanol Fuel Cells

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We have made polyvinylalcohol membranes containing mordenite which have twenty times better selectivity for protons over methanol than perfluorinated sulfonic acid polymers. Membranes like these should improve the efficiencies of fuel cells fed directly with methanol. Our results show that further improvements are possible with composite membranes, but that these improvements will require polymers less conductive than those currently used. This is the opposite of conventional wisdom.  
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Fuel cells are attractive power sources because they convert chemical energy into mechanical or electrical energy without the constraint of a Carnot efficiency.<sup>1</sup> This means that, in principle, the efficiency of a fuel cell-based automobile could be more than twice that of one using a conventional internal combustion engine. While fuel cells date from 1839, recent advances in catalysis make these devices much more practical.

The best current fuel cells are fed with hydrogen, which reacts at the anode to produce electricity and protons. The protons then diffuse across a 200  $\mu\text{m}$  perfluorinated polysulfonic acid membrane (like Nafion), where they react with oxygen to produce water. The cells work well, but require a source of hydrogen, which is difficult to store. Efforts with alternative fuels often reform hydrocarbons, producing hydrogen with at least traces of carbon monoxide. Unfortunately, carbon monoxide fouls the anode catalyst.<sup>2</sup> Efforts to separate this gaseous mixture usually depend on a palladium membrane, which is permeable to hydrogen but not to other gases. Although this palladium membrane works, it is expensive, must be very thin, and runs best above 300°C.<sup>3</sup>

As an alternative, we can build fuel cells which burn methanol and other hydrocarbons **directly**, without first making hydrogen. Such cells do work, but **they have** only ~50% of the output of hydrogen based fuel cells.<sup>4</sup> This loss of power is largely due to methanol leaking across the polysulfonic acid membrane, where it reacts at the cathode, producing no electricity and fouling the cathode catalyst. To reduce the effects of this leak, direct methanol fuel cells are currently fed with only a 2% solution of methanol.<sup>5</sup>

A successful methanol fuel cell requires a membrane that is both an effective proton conductor and methanol barrier. To be more specific, membranes must be highly selective for protons over methanol. Selectivity for most separation processes is defined as the ratio of fluxes to driving forces for the two species. For a methanol fuel cell membrane, the driving forces for protons and methanol are different, so selectivity  $\beta$  is defined as

$$\beta = \frac{i/j}{\Delta\Phi/\Delta c} \quad [1]$$

where  $i$  is the current density,  $j$  is the methanol flux,  $\Phi$  is the electrostatic potential, and  $\Delta c$  is the methanol concentration difference. Current density  $i$  and methanol flux  $j$ , respectively, can be further defined as

$$i = \sigma(\Delta\Phi/l) \quad [2]$$

$$j = P(\Delta c/l) \quad [3]$$

where  $\sigma$  is the proton conductivity,  $P$  is the methanol permeability, and  $l$  is the membrane thickness. Substituting yields the selectivity  $\beta$  as

$$\beta = \frac{\sigma}{P} \quad [4]$$

Note that  $\beta$  is independent of the membrane thickness. Our goal is to develop a methanol fuel cell membrane with improved selectivity vs. Nafion.

We can attack this goal in three ways. First, we can use membranes made of polymers like polyvinylalcohol which are known to be selective for water vs. methanol. Most such membranes have a lower conductance than the 0.1 S/cm of the 200  $\mu\text{m}$  Nafion membrane. We can recover the low resistance by using a thinner membrane of these new, more selective polymers. After all, commercial membrane separations routinely make membranes whose selective layers are 0.1-1  $\mu\text{m}$ .<sup>6</sup> However, our efforts with these new polymers have failed: polymers whose methanol permeability varied 10,000 times have the same proton to methanol selectivity.<sup>7</sup>

Second, we can seek better proton vs. methanol selectivity by using solid membranes with pores large enough to pass protons but small enough to stop methanol. Such pores, often based on zeolites, are actively pursued for gas separations and reactions.<sup>8</sup> The pores' selectivity is **based not only on size**, but also on chemical interactions. However, we felt that submicrometer sheets of zeolite would be excessively fragile and expensive. We chose not to pursue this route.

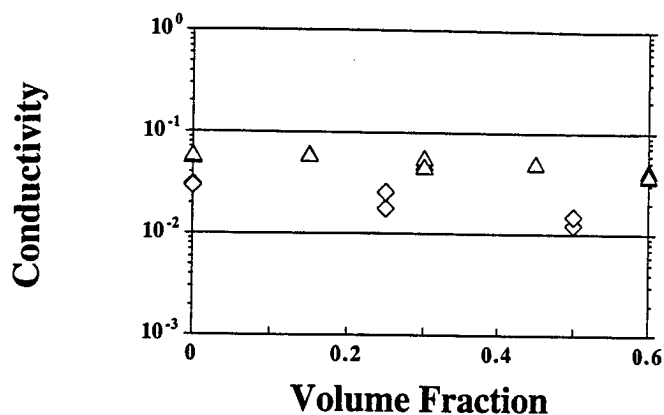
Third, we can seek better selectivity through a composite membrane of a conducting polymer containing selective zeolite particles. Such membranes show modest selectivity enhancements for water from azeotropic ethanol-water solutions and for oxygen from air.<sup>9,10</sup> We synthesized composite membranes consisting of mordenite particles in a polyvinylalcohol (PVA) matrix. The hydrophilic nature of both PVA and mordenite prevent the formation of nonselective voids at the polymer-zeolite interface, while also allowing mordenite to be selective for protons over methanol. Additionally, mordenite is one of the most stable zeolites in existence, has one of the highest proton conductivity values among zeolites ( $\sim 10^{-3}$  S/cm), and has been studied before for methanol fuel cell applications.<sup>11,12</sup> Membranes were cast from a 5% aqueous solution of PVA (Elvanol 71-30, DuPont, Wilmington, DE) containing 2-4  $\mu\text{m}$  mordenite (HM 40,  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 40$ , Sud-Chemie, Louisville, KY). After the membranes were air dried, they were heat-treated at 150°C for 1 or 27 h. Micrographs of cross sections of these membranes show that the mordenite particles are evenly distributed. After a 24 h hydration, they were equilibrated with 1 M  $\text{H}_2\text{SO}_4$  to enhance the conductivity of both PBA and mordenite. Their conductance was measured with an impedance instrument (Solartron model 1286), and their methanol permeability was determined with a diaphragm cell fitted with a differential refractometer (Waters model 410, Framingham, MA).

Figures 1 and 2 display the proton conductivity and methanol permeability results, respectively, for these membranes as a function of the volume fraction of mordenite. For comparison purposes, the proton conductivity of Nafion 117 is  $\sim 0.11$  S/cm and its methanol permeability is  $\sim 2.5 \times 10^{-6}$   $\text{cm}^2/\text{s}$ . Utilizing the previously out-

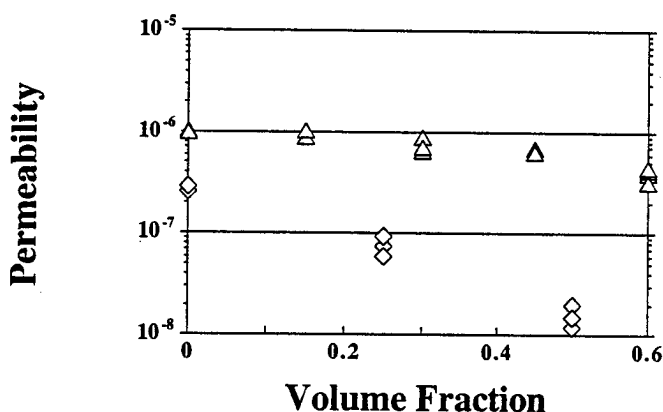
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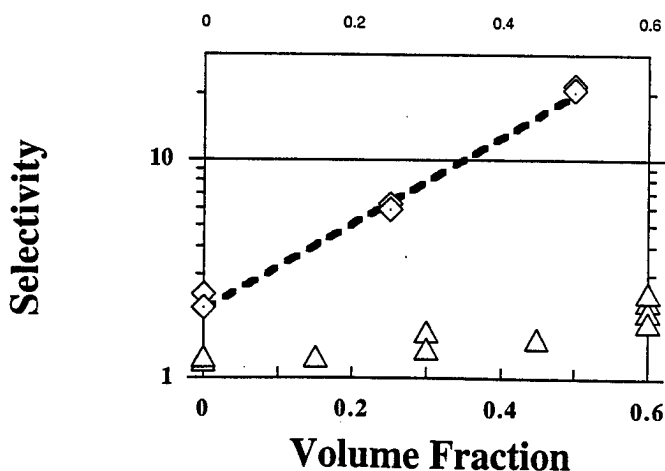


**Figure 1.** Proton conductivity (S/cm) vs. mordenite concentration. For both the short heat-treatment ( $\Delta$ ) and the long heat-treatment ( $\diamond$ ), the conductivity drops slightly as the mordenite content increases.

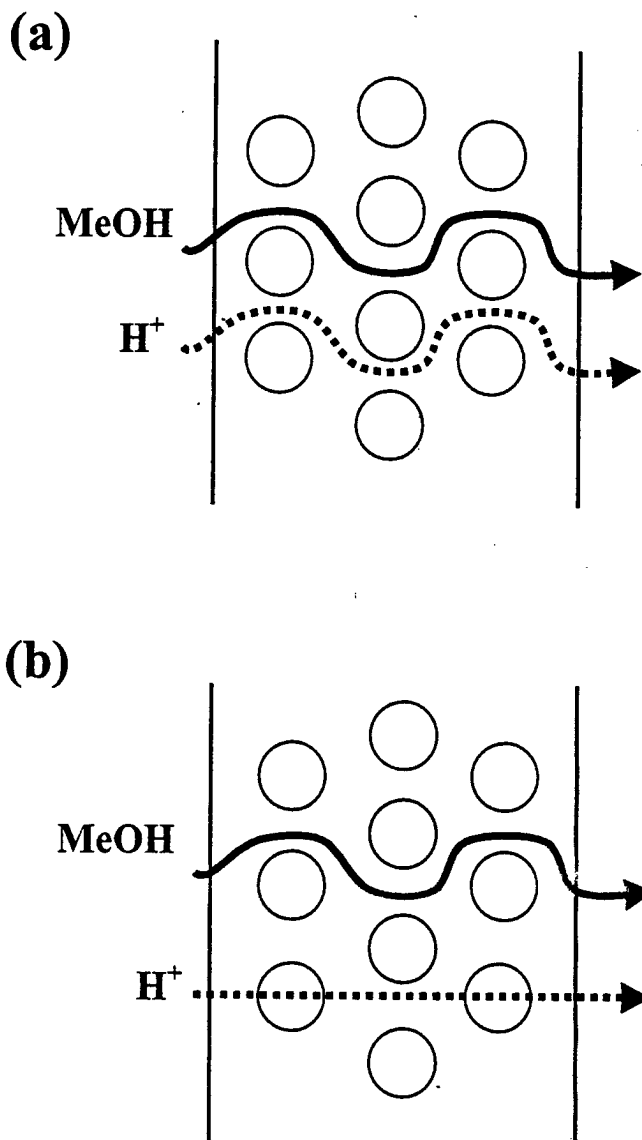


**Figure 2.** Methanol permeability (cm<sup>2</sup>/s) vs. mordenite concentration. For a short heat-treatment ( $\Delta$ ), permeability demonstrates a 2.5-fold reduction over the mordenite concentration range. In contrast, the long heat-treatment ( $\diamond$ ) causes permeability to decrease 25 times.

lined selectivity analysis, the conductivity and permeability results are combined to yield the selectivity data shown in Fig. 3. The ordinate is the selectivity of the composite membrane for protons vs. methanol relative to the selectivity of Nafion 117. As can be seen,



**Figure 3.** Selectivity relative to nafion vs. mordenite concentration. For a short heat-treatment ( $\Delta$ ), the mordenite changes the selectivity only two times. For the longer heat-treatment ( $\diamond$ ) the selectivity increases 20 times.



**Figure 4.** Schematic showing why the membrane is selective. The mordenite particles are less permeable than the surrounding continuum in (a), but are more permeable than the continuum in (b).

the selectivity of the membranes treated for 1 h increases only modestly as the concentration of mordenite increases. The selectivity of the membranes treated for 27 h increases twenty times for a membrane which is 50 vol % mordenite.

The reasons why this longer heat-treatment increases the selectivity are not immediately obvious. The 27 h heating reduces the methanol permeability 40 times compared with the 1 h heating. It reduces the proton conductivity four times. These decreases are almost certainly the result of membrane dehydration and cross-linking, which can be clearly seen from IR spectra (Nicolet Magna-112 model 550). These reactions are catalyzed by the acid functionalities of the mordenite.<sup>13</sup> Membranes heat-treated without mordenite do not show these changes in spectra, but membranes heat-treated in 0.01 M H<sub>2</sub>SO<sub>4</sub> are almost identical with the composite films with mordenite. However, membranes heated with 0.01 M H<sub>2</sub>SO<sub>4</sub> do not show improved selectivity.

We believe that the mordenite has two roles in improving the proton to methanol selectivity. First, it catalyzes the reactions which reduce the permeability. Second, mordenite provides an easy pathway for protons. The result is shown schematically by Fig. 4. With only 1 h heat-treatment, both protons and methanol go around the mordenite particles, as shown in Fig. 4a. While these particles are

selective, they are much less conductive than the polymer. In contrast, after the 27 h heat-treatment, protons shuttle through the mordenite, but methanol still is forced to go around. Thus the composite membrane becomes more selective.

We can put these ideas on a more quantitative basis by using the calculations of Maxwell for an insulator containing a periodic array of conducting spheres.<sup>14</sup> Although Maxwell's equations are accurate only for dilute suspensions, they are effective for membranes made more selective for oxygen with high concentrations of porous carbon.<sup>10</sup> For protons moving through a polymer containing infinitely conducting spheres

$$\frac{\sigma}{\sigma_0} = \frac{1 + 2\phi}{1 - \phi} \quad [5]$$

where  $\sigma$  and  $\sigma_0$  are the proton conductivities of the composite and of the pure polymer, and  $\phi$  is the volume fraction of spheres. For methanol moving through a polymer containing infinitely impermeable spheres

$$\frac{P}{P_0} = \frac{2(1 - \phi)}{2 + \phi} \quad [6]$$

where  $P$  and  $P_0$  are the methanol permeabilities of the composite and the pure polymer, respectively. The selectivity ( $\sigma/P$ ), easily found by combining these equations, is shown by the dotted line in Fig. 3. This prediction, which contains no adjustable parameters, agrees closely with the experimental results.

We recognize that the composite membrane made in this work is not the perfect solution for direct methanol fuel cells. While it is, almost literally, as cheap as dirt, the fact that it must be doped with acid will cause major operational problems, especially involving corrosion. However, this work does show how composite membranes can be made which are more selective than Nafion. First, the polymer must wet any solid particles to prevent the formation of nonselective voids at the interface. Second, both polymer and par-

ticles must have fixed negative charges to remove the need for doping. Third, the particles should conduct protons as fast as possible. Finally, the polymer should be less conductive than those in present use to take advantage of the selectivity of the particles. In our case, the polymer should have conductivity about a hundred times less than the particles. In general, however, the Maxwell analysis suggests a more complex result. Note that the conclusion that lower proton conductivity is needed for more selective composite membranes is the antithesis of much current effort, which seeks more conductive polymers.

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#### References

1. A. J. Appleby and F. R. Foulkes, *Fuel Cell Handbook*, p. 1, Van Nostrand Reinhold, New York (1989).
2. S. Wasmus and A. Kuver, *J. Electroanal. Chem.*, **461**, 14 (1999).
3. J. Han, I. Kim, and K.-S. Choi, *J. Power Sources*, **86**, 223 (2000).
4. X. Ren, M. S. Wilson, and S. Gottesfeld, *J. Electrochem. Soc.*, **143**, L12 (1996).
5. C. K. Dyer, *Sci. Am.*, **280**, 88 (1999).
6. W. S. W. Ho and K. K. Sirkar, *Membrane Handbook*, Van Nostrand Reinhold, New York (1992).
7. B. S. Pivovar, Y. Wang, and E. L. Cussler, *J. Membr. Sci.*, **154**, 155 (1999).
8. J. Caro, M. Noack, P. Kolsch, and R. Schafer, *Microporous Mesoporous Mater.*, **38**, 3 (2000).
9. Z. Gao, Y. Yue, and W. Li, *Zeolites*, **16**, 70 (1996).
10. C. M. Zimmerman, A. Singh, and W. J. Koros, *J. Membr. Sci.*, **137**, 145 (1997).
11. D. W. Breck, *Zeolite Molecular Sieves: Structure, Chemistry, and Use*, John Wiley & Sons, New York, (1974).
12. N. Rao, T. P. Andersen, and P. Ge, *Solid State Ionics*, **72**, 334 (1994).
13. J. G. Pritchard, *Poly(vinyl alcohol) Basic Properties and Uses*, p. 81, Gordon and Breach Science Publishers, London (1970).
14. J. C. Maxwell, *Treatise on Electricity and Magnetism*, Vol. 1, p. 365, Clarendon Press, Oxford (1873).

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